

PATENT SPECIFICATION

(11) 1211302

1211302

DRAWINGS ATTACHED

(21) Application No. 5831/68 (22) Filed 6 Feb. 1968
(31) Convention Application No. 614 151 (32) Filed 6 Feb. 1967 in
(33) United States of America (US)
(45) Complete Specification published 4 Nov. 1970
(51) International Classification C 01 f 11/46
(52) Index at acceptance

C1A D45 G46 G46D45
B2E 191 193 197 19Y 209 20Y 229 327 349 41X 41Y 429
44Y 473 485 498 541 568 658
G2J 15 X17

(72) Inventors FRANC GRUM, GEORGE WILLIAM LUCKEY and
GEORGE PALMER WAUGH



(54) BARIUM SULPHATE REFLECTANCE STANDARDS

(71) We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester, New York 14650, United States of America do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with spectrophotometers, methods of determining the reflectance characteristics of samples by means of a spectrophotometer and a novel reflectance standard and its method of preparation.

The present invention provides a reflectance standard useful for reproducible spectroreflectometric measurements and so has the advantage that the spectrophotometer does not have to be recalibrated frequently. The reflectance standards of the present invention also give good reflectance in the 200 nm to 400 nm part of the spectrum.

According to the present invention there is provided a process for the preparation of barium sulphate which comprises adding simultaneously an aqueous solution of barium chloride and a solution formed by dissolving sodium chloride and sulphuric acid in water, to a further solution formed by dissolving sodium chloride and sulphuric acid in water, the reaction mixture being maintained at a pH of less than 2 and a temperature greater than 50°C throughout the reaction.

The process of preparation of barium sulphate according to the present invention provides a means of producing a high-purity barium sulphate which has a very low concentration of impurities which absorb incident light having wavelengths in the range from 200 nm to 2500 nm. Preferably, the concentration of such impurities is less than 5 parts in a million

of BaSO₄. Further, the process employs the double jet method of precipitation which allows the particle size of the barium sulphate produced to be closely controlled, preferably in a range from 0.05 to 3.0 microns. The BaSO₄ produced is usually washed with distilled water and vacuum dried at a temperature above 100°C. The double jet method for the preparation of barium sulphate is described, for example, in U.S. Patent No. 2,358,050. Barium sulphate powder prepared according to the invention having a content of from 0.5% to 7% water can be mixed with polyvinyl alcohol in varying proportions preparatory to producing either a plaque or a coating composition. Polyvinyl alcohol prepared by a continuous method as described in U.S. Patents 2,642,419 and 2,643,994, with properties similar to the material described in Example 22 of U.S. 2,642,420 is of particular value when combined with the high-reflectance barium sulphate of this invention. When barium sulphate is used in formulations containing from 100 to 500 parts by weight of barium sulphate to one part of such a polyvinyl alcohol, a coating composition and a plaque for use as a reflectance standard can be prepared. In particular, a suitable coating composition can be compounded by dispersing about 150 parts of barium sulphate and about one part of polyvinyl alcohol in a selected amount of a carrier to produce a coating composition of the desired consistency for coating. Such a composition can be applied to the interior of an integrating sphere by any suitable technique such as by spraying, bulk coating or brush application. Likewise, a composition comprising barium sulphate having a moisture content as hereinbefore described can be compounded with polyvinyl alcohol in a weight ratio of at least 100 parts of barium sulphate to one part of polyvinyl alcohol and the resulting composi-

[Price 5s. Od. (25p)]

ti n pressed in a suitable compression device to a density in the range of 2 to 4 grams per cm³ to produce a substantially perfect matte-finish plaque having a reflectance in the range of wavelengths from about 200 to 2,500 cm. Similarly, barium sulphate prepared according to the invention can be compressed into a plaque having a density in the range from 2 to 4 grams per cm³, in the absence of polyvinyl alcohol.

When the coating composition and plaque are used in combination in a spectrophotometer for the comparative measurement of reflectances of samples the combination produces results of high accuracy and reproducibility in the range of wavelengths in nanometers from 200 nm to 2,500 nm.

The use of barium sulphate prepared according to this invention as a reflectance standard is illustrated in the accompanying drawings, in which:

Figure 1 is a schematic illustration of an instrument for spectroreflectometrically measuring the reflectance of samples against a reference standard in a coated light-integrating sphere.

Figure 2 is a graph of the percentage reflectance of a barium sulphate-containing plaque used as standard in this invention.

Figure 3 is a graph of the percentage of reflectance of a reflectance standard containing magnesium oxide, (a) freshly prepared, (b) two days old, and (c) 11 weeks old.

In the drawings, Figure 1 illustrates a monochromator housing 1 of the reflectance-comparing unit wherein a radiant energy source 2 originates a beam 2A which is reflected from a mirror 2B through an entrance slit 3 where it is again reflected from a mirror 4 to a dispersing prism 4A back to the collimating mirror 4 and then through an exit slot 5 to a beam chopper 6. The beam chopper 6 alternately splits or chops the beam 2A into the two components illustrated. One of the components is reflected from a mirror 6A into an integrating sphere 7 in line with a sample positioned at a sample port 9. A mirror 6B reflects the second beam into the integrating sphere 7 in line with a reference positioned at a reference port 8. The energy reflected from the materials positioned at the reference port 8 and the sample port 9 respectively are alternately compared by a detector 10, which may be, for example, a photomultiplier tube or a photoelectric cell. The signals are then compared in some appropriate manner, for example, graphically on a recorder (not shown). In operation, a spectroreflectometric determination depends on the total energy impinging upon the detector 10. Normally the energy level is held constant by providing the exit slit 5 with a variable aperture whose size is changed by an aperture control means 11 which controls the size of the aperture at the exit slot 5 by being responsive to the energy

received by the detector 10. In this manner when the total energy reflected from all points of the light integrating sphere 7 diminishes owing to deterioration of the internal coating of the sphere 7 or from deterioration of the reference standard, the detector 10 will respond by signalling the aperture control means 11 which changes the aperture of the exit slit 5 to increase the amount of total energy entering the integrating sphere 7 so as to maintain the relative differences in reflectances between the reference standard and the sample to be compared. It can be seen from this type of instrumental setup that a deterioration in either the coating for the sphere 7 or the reference standard at the reference port 8 will increase the aperture at the exit slit 5 thereby decreasing the effective resolution of the instrument, particularly in the shorter wavelengths. It is this weakness in the instrument which has necessitated frequent renewal of the coating for the inside of the integrating sphere 7 and renewal of the reference plaque at the reference port 8 when MgO has been used as a reflectance standard. Such changes must, of course, be accompanied by recalibration of the instrument. Thus the deterioration of the standard plaque or of the coating of the sphere, diminishes the useful wavelength range of the instrument.

The frequency with which an instrument must be recalibrated can be determined roughly by reference to Figure 3. The curves in Figure 3 clearly show that magnesium oxide loses the desired reflectance response in a relatively short period of time in the critical portions of the spectrum between 200 and 400 nm. As the magnesium oxide deteriorates, the resolution of the reflectance from samples measured in this region of wavelengths is severely restricted.

The useful range of the instrument designed for 2,500 nm down to 200 nm will not be restricted by the use of a barium sulphate-containing reference standard prepared according to this invention when used in an integrating sphere, such as the integrating sphere 7, Figure 1 of the drawings, which has been coated with a preparation comprising a similar high-reflectance barium sulphate-containing material.

The following Examples 1 to 4 illustrate the method of preparation of barium sulphate according to the invention.

EXAMPLE 1

A quantity of reagent grade barium chloride dihydrate, was dissolved in distilled water to make a 1.35 molar solution. This solution was set aside for 2 hours, before 925 ml. of it were decanted into a calibrated flask and diluted with enough distilled water to make 5 litres. (Solution 1A). Solution 1A was then heated to 70°C.

A quantity of reagent grade sodium chloride was dissolved in distilled water to make a 3

130

5 molar solution. This solution was also set aside for 2 hours. Another solution was prepared by mixing 417 ml. of 3 molar sulphuric acid (prepared from reagent grade sulphuric acid and distilled water) and 400 ml. of decanted 3 molar sodium chloride with sufficient distilled water to make 5 litres of solution (Solution B). Solution B was also heated to 70°C.

10 Solutions A and B were each added simultaneously at a rate of 333 ml. per minute into a third solution which had been prepared by mixing 200 ml. of 3 molar sulphuric acid solution and 200 ml. of 3 molar sodium chloride solution with sufficient water to make 4 litres.

15 This latter solution had been previously heated to its boiling point before the start of the reac-

tion. During the reaction the solution was thoroughly agitated with a stirrer. Throughout the reaction the pH of the reaction mixture was less than 1. At the conclusion of the reaction the supernatent liquid was poured off and the precipitate washed four times by decantation with cold distilled water. The precipitate was collected on a suction filter and dried at 120°C. in a vacuum oven. The dried powder was pressed in a receptacle, 1.375 inches in diameter and 3/8 of an inch deep and then compared with a freshly prepared magnesium oxide surface in a Beckman DK-2A spectrophotometer. The results of these tests are shown in Table I.

TABLE I

Wavelength in nm.	700	600	500	400	300	250
Reflectance of BaSO ₄ relative to fresh MgO	+1.8%	+1.4%	+1.2%	+2.5%	+4.1%	+5.3%

EXAMPLE 2

35 A 1.35 molar solution of barium chloride was prepared as described in Example 1. A 925 ml. portion of this solution was then diluted with sufficient distilled water to make 5 litres of solution A which was then heated to 70°C. Five litres of sulphuric acid-sodium chloride solution B were prepared as described in Example 1 and the solution heated to 70°C. The two solutions were then added simultaneously at a rate of 33.3 ml. of each per minute to a solution previously prepared by mixing

45 800 ml. of 3 M sulphuric acid solution and 200 ml. of 3 M sodium chloride solution with sufficient distilled water to make 4 liters. This solution was heated to its boiling point before starting the reaction as described in Example 1. At the conclusion of the reaction, the precipitate was washed, collected, dried and pressed into a receptacle and compared with a freshly prepared MgO surface in a Beckman DK-2A spectrophotometer as in Example 1. The results of these tests are shown in Table II.

50

55

TABLE II

Wavelength in nm.	700	600	500	400	300	250
Reflectance of BaSO ₄ relative to fresh MgO	+1.2%	+1.0%	+1.2%	+1.9%	+5.2%	+7.0%

EXAMPLE 3

60 Example 1 was repeated, with the modification that the solutions A and B were added to the solution C at a rate of 833 ml. of each per minute. The precipitate was washed, collected, and dried as described in Example 1.

The dried powder was pressed into a receptacle and compared with a freshly prepared MgO surface in a Beckman DK-2A Spectrophotometer as in Example 1. The results of these tests are shown in Table III.

65

TABLE III

Wavelengths in nm.	700	600	500	400	300	250
Reflectance of BaSO ₄ relative to fresh MgO	+1.8%	+1.4%	+1.2%	+2.5%	+4.5%	+6.0%

5 The barium sulphate powder in the receptacle and the magnesium oxide were then exposed for 24 hours to the radiation from a 6000 watt "Osram" Xenon arc lamp at a dis-

tance of 11.5 feet. The reflectances of the two coatings after exposure are summarized in Table IV.

TABLE IV

Wavelength in nm.	700	600	500	400	300	250
Reflectance relative to fresh BaSO ₄ :						
for MgO after exposure —	-0.4%	-0.4%	-0.6%	-0.8%	-2.0%	-4.0%
Reflectance relative to fresh BaSO ₄ :						
for BaSO ₄ after exposure —	-0%	-0%	-0%	-0%	-0.8%	-1.5%

10 The results in Table IV show that the barium sulphate is more stable than magnesium oxide when exposed to the "Osram" Xenon arc. The exposed magnesium oxide layer was stored in the dark at 23°C. and at a relative humidity of 45% for 10 days. After this storage, the

% changes in reflectance shown in Table V were obtained. The exposed barium sulphate pressing was kept under the same conditions for 110 days. The % changes in reflectance after this storage are also shown in Table V.

20

15

TABLE V

Wavelength in nm.	225	250	300	400	500	600
Magnesium oxide (10 days)	-8.0	-2.0	-1.0	-0.4	-0.3	-0.2
Barium sulphate (110 days)	-0.9	-0.8	-0.6	-0.4	-0.3	-0.2

25 The results in Table V show that the barium sulphate pressing is more stable than the magnesium oxide layer when stored under ambient conditions.

EXAMPLE 4

30 A 1.155M solution of barium chloride was prepared as described in Example 1. Then 1080 ml. of this solution were filtered and diluted with distilled water to make 5 liters and

the solution heated to a temperature of 70°C. A second solution was prepared by mixing 417 ml. of 3M sulfuric acid and 250 ml. of 3M sodium chloride solution with sufficient distilled water to make 5 liters of solution. This solution was also heated to a temperature of 70°C. The two solutions were then added simultaneously at a rate of 333 ml./min. to a third solution prepared by mixing 400 ml.

35

of the 3M sulfuric acid solution with 100 ml. of 3M sodium chloride solution and sufficient water to make 4 liters. This solution was heated to its boiling point before starting the reaction in a 22-liter round bottom flask in the manner described in Example 1. The product was washed, collected, and dried as described in Example 1. This procedure was repeated with 500 ml. of sodium chloride solution in the second solution and 200 ml. of sodium chloride solution in the third solution. It was further

repeated with 125 ml. of sodium chloride solution in the second solution and 50 ml. of sodium chloride solution in the third solution. It was still further repeated with 62.5 ml. of sodium chloride solution in the second solution and 25 ml. of sodium chloride solution in the third solution. When the dried powders were placed in the receptacle and tested as described in Example 1, the results summarized in Table VI were obtained.

15

20

TABLE VI

Wavelength in nm.	700	600	500	400	300	250	225
Reflectance of BaSO ₄ relative to fresh MgO in % for 250/100 NaCl	+2.3	+1.6	+2.2	+3.4	+6.8	+8.3	+32.3
500/200 NaCl	+2.2	+1.6	+2.0	+2.6	+6.3	+7.7	+31.5
125/50 NaCl	+2.1	+1.5	+2.0	+2.8	+6.4	+8.2	+32.4
62.5/25 NaCl	+1.9	+1.5	+2.0	+2.6	+6.6	+8.2	+32.3

After making these measures, the samples of powder were placed 1.5 feet from a 6000 watt "Osram" Xenon arc lamp and exposed for 48 hours. After exposure, the reflectances of the samples were measured as before. The results are shown in Table VII.

25

TABLE VII

Wavelength in nm.	700	600	500	400	300	250	225
Reflectance of BaSO ₄ relative to fresh MgO in % for:							
250/100 NaCl	+2.2	+1.5	+2.1	+2.8	+5.1	+4.7	+26.5
500/200 NaCl	+2.2	+1.6	+1.9	+2.6	+4.6	+4.5	+26.4
125/50 NaCl	+2.2	+1.6	+1.8	+2.7	+4.5	+4.8	+26.5
62.5/25 NaCl	+2.0	+1.7	+1.8	+2.7	+4.8	+4.8	+26.9

30 The infrared reflectances of these barium sulphate samples were compared with that of thermally deposited magnesium oxide. This comparison is shown in Table VIII. The samples were not exposed to the Xenon arc lamp before making the measurements.

35

TABLE VIII
(Near-Infrared Reflectance)

Wavelength in nm.	2400	2200	2000	1800	1600	1400	1200	1000	800
Reflectance of BaSO_4 relative to fresh MgO in % for:									
250/100 NaCl	+92.2	+95.0	+91.8	+99.1	+100.1	+99.9	+102.2	+102.5	+102.5
500/200 NaCl	+92.3	+95.0	+91.8	+99.0	+100.1	+99.8	+101.9	+102.4	+102.4

5 Satisfactory barium sulphate powders have been made with a wide range of concentration of sulphuric acid in the reactor. The concentration of acid is preferably selected to yield a product with grain sizes substantially in the range from 0.05 to 3 microns.

10 Grain sizes in the range from 0.05 to 3 microns are achieved by maintaining the level of sulphuric acid in the reaction mixture during the reaction at a level such that the barium sulphate retains the same degree of solubility during the reaction as in the initial reaction solution. If the BaSO_4 becomes too soluble 15 in the reaction mixture then a large proportion of grains larger than 3 microns in size are produced, and conversely, if the BaSO_4 becomes too insoluble in the reaction mixture a large proportion of grains smaller than 0.05 microns in size are produced. The solubility 20 of the BaSO_4 increases as the concentration of hydrogen ions increases.

25 The composition of the reaction mixture can be adjusted by varying the rates at which reagents are added to it. For producing BaSO_4 grains in the desired size range a sulphate ion concentration in the range from 0.15M to 0.6M and a hydrogen ion concentration in the range from 0.3M to 1.2M are the preferred concentrations of these ions in the reaction 30 mixture. For example, a concentration of about 0.3M sulphate ion and about 0.6M hydrogen ion in the reaction mixture is particularly useful for producing grains in the desired size range.

35 A preferred range of concentration of sodium chloride in the reaction mixture is from 0.015M to 0.15M. Particularly useful for producing BaSO_4 having a good reflectance properties is a NaCl concentration of about 0.075M in the reaction mixture.

40 Powders which have grains larger than 3 microns have poorer reflectances, although the values are still greater than those of MgO in

some regions of the ultraviolet spectrum. Powders with grain sizes smaller than 0.05 micron have good reflectances when dry, but they are difficult to wash thoroughly and they are sensitive to changes in the relative humidity of their surroundings.

45 The preparation of pigmented plaques and coating compositions, containing barium sulphate prepared according to this invention, which are used in combination to form reflectance standards is illustrated below.

EXAMPLE 5

50 Barium sulphate powder (100 grams) prepared by the method described in Example 1 was milled with 65 ml. of 3A ethanol 55 (19:1:1 mixture of ethanol, methanol, and water, respectively, by volume) in a glass mortar. Then 35 ml. of distilled water and 20 ml. of a 5% solution of polyvinyl alcohol in water were added and the mixture was thoroughly stirred. After stirring, the mixture was 60 coated on a grained aluminum sheet at a coverage of 0.040" wet thickness, and dried at room temperature. Another sample of the 65 mixture was placed in a spray gun ("DeVilbiss" spray gun Type MBC, nozzle No. 30 70 at 45—60 psi air pressure) and sprayed onto a steel hemisphere which had been previously 75 coated with a layer of a suitable material (flat white paint) for adhesion of the coating to the steel. Three coats were applied allowing 10 min. drying between coatings in a well-ventilated booth. The polyvinyl alcohol used in 80 making this dispersion was prepared by the following method: A 30 percent solution of medium viscosity poly(vinyl acetate) in methanol (containing 7.6 per cent water by weight) was mixed with one-tenth its volume of a 10 percent solution of sodium hydroxide in methanol. The gel which soon formed was presently 85 cut into small pieces (1/4 to 1/2 inch). These were soaked in water, washed in more water, soaked in 0.2N sodium hydroxide overnight,

further washed in water, soaked overnight in 1N hydrochloric acid, and washed in distilled water until neutral. The reflectance of these

coatings was compared with that of a freshly prepared magnesium oxide surface in a Beckman DK-2A spectrophotometer.

5

TABLE IX

Wavelength in nm.	800	700	600	500	400	300	250	225
Reflectance of BaSO₄ containing composition relative to fresh								
MgO								
	+1.2%	+0.9%	+0.5%	+0.6%	+0.8%	+1.0%	+1.0%	+15.0%

After making these measurements, the coating on aluminum foil was placed 1.5 feet from a 6000 watt "Osram" Xenon arc lamp and exposed for 24 hours.

A sample of magnesium oxide prepared by

the method of thermal deposition was placed adjacent to the coating during the exposure. The reflectances of these samples after exposure were measured as before and the results are summarized in Table X.

15

TABLE X

Wavelength in nm.	700	600	500	400	300	250	225
Decrease in reflectance							
BaSO ₄ coating	0.2%	0.1%	0.1%	0	0.4%	0.2%	0
Fresh MgO	0.2%	0.2%	0.4%	0.2%	2.0%	5.7%	6.0%

When plaques containing barium sulphate pigment prepared in a manner similar to Example 1 were formed from compositions containing one part by weight of polyvinyl alcohol as in Example 5, and 100 to 200 parts by weight of barium sulphate containing about 0.5% to about 7% by weight of water, the preferred mode of formation was under 3000 to 4000 psig. The preferred density of the compacted material ranged from 2 to 4 grams per cubic cm. This density also provides the reference plaque with the most desirable mechanical strength although high reflectance material can be produced according to this invention having less desirable properties by using ratios and densities outside of the preferred range.

"Osram" and "DeVilbiss" are Registered Trade Marks.

action mixture being maintained at a pH of less than 2 and a temperature greater than 50°C. throughout the reaction.

2. A process as claimed in Claim 1, in which the concentration of sodium chloride in the reaction mixture is maintained in the range from 0.015 to 0.15M.

50

3. A process as claimed in either Claim 1 or 2 in which the concentration of sulphuric acid in the reaction mixture throughout the reaction is maintained such that the barium sulphate formed has grain sizes in the range from 0.05 to 0.3 microns.

55

4. A process as claimed in Claim 3, in which the concentration of sulphuric acid in the reaction mixture is maintained at a level such that the concentration of sulphate ion is in the range from 0.15M to 0.6M and the concentration of hydrogen ion is in the range from 0.3M to 1.2M.

60

5. A process for the preparation of barium sulphate substantially as described in any of Examples 1 to 7 herein.

65

6. Barium sulphate whenever prepared by a process according to any of claims 1 to 5.

70

7. A composition comprising from 100 to 500 parts of BaSO₄ as claimed in Claim 6, and 1 part of polyvinyl alcohol.

WHAT WE CLAIM IS:—

1. A process for the preparation of barium sulphate which comprises adding simultaneously an aqueous solution of barium chloride and a solution formed by dissolving sodium chloride and sulphuric acid in water, to a further solution formed by dissolving sodium chloride and sulphuric acid in water, the re-

8. A plaque for reflectometric measurements prepared by compressing BaSO₄ as claimed in Claim 6, or a composition as claimed in Claim 7, to a density in the range from 2 to 4 grams per c.c.

5 9. A reflectance standard for use in spectrophotometers which comprises a plaque as claimed in Claim 8 and a coating of a composition as claimed in Claim 7.

10 10. A spectrophotometer comprising an integrating sphere having a reflectance standard as claimed in Claim 9.

11. A spectrophotometer comprising an integrating sphere having a reflectance standard as claimed in Claim 9, substantially as illustrated in the accompanying Fig. 1.

12. A method of measuring the reflectance of a sample material which comprises using a reflectance standard as claimed in Claim 9, in the integrating sphere of a spectrophotometer.

L. A. TRANGMAR, B.Sc. C.P.A.
Agent for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1970.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

1211302

COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of
the Original on a reduced scale

Fig.1.

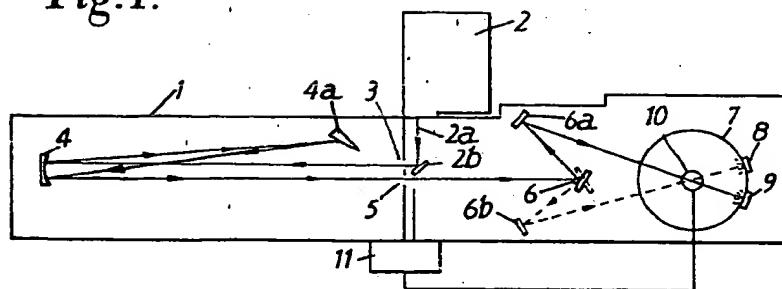


Fig.2.

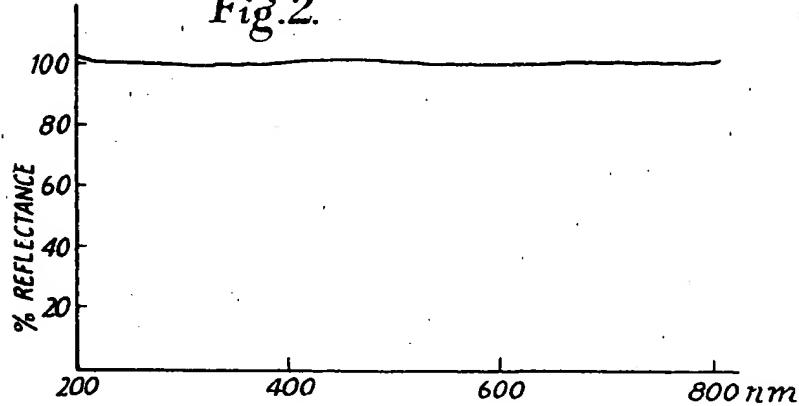
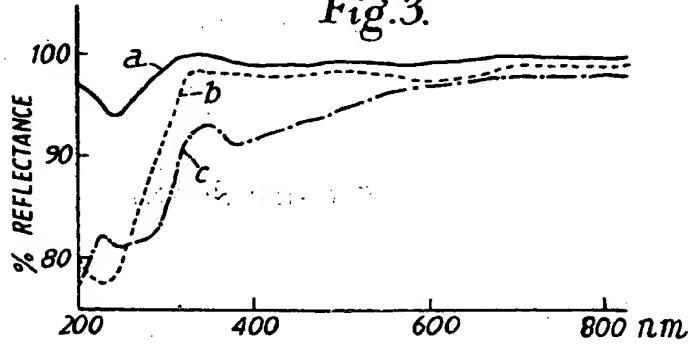


Fig.3.



THIS PAGE BLANK (USPTO)